AFOSR-TR-97

0151

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 03/13/97	3. REPORT TYPE AND DATES COVERED Final Report 01/15/94-01/14/97

4. TITLE AND SUBTITLE

Transition State Spectroscopy by Photodetachment of Vibrationally Excited Atoms

5. FUNDING NUMBERS

2303/ES
61102F

6. AUTHOR(S)

Daniel M. Neumark

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of California
Sponsored Projects Office
336 Sproul Hall
Berkeley, California 94720-5940

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Office of Scientific Research/NL
Chemistry and Materials Science Research
110 Duncan Avenue, Suite B115
Bolling Air Force Base, DC 20332-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

F49620-94-1-0115

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The research supported by this grant centers on the spectroscopy and dynamics of a variety of transient species including transition states, clusters, and free radicals. These species lie at the heart of many chemical processes, and our experiments have provided unpresedented insight into their nature. The novel feature of this program is that negative ion spectroscopy is used as the basic experimental tool in all of these experiments, because in many cases negative ions provide the only way to generate the transient species of interest in a reasonably well-defined manner. The projects described fall into three categories: (a) spectroscopy of the transition state and reactive intermediates for neutral, bimolecular reactions, (b) the spectroscopy and electron detachment dynamics of carbon cluster anions, and (c) studies of size-selected, weakly bound anion and neutral clusters.

DTIC QUALITY INSPECTED 4

14. SUBJECT TERMS

transition states, clusters, radicals, photodetachment

15. NUMBER OF PAGES

7

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UNLIMITED (SAR)

FINAL TECHNICAL REPORT

TITLE: Transition State Spectroscopy by Photodetachment of Vibrationally Excited Atoms

PRINCIPAL INVESTIGATOR: Daniel M. Neumark

DATE: January 15, 1994 - January 14, 1997

GRANT NO: F49620-94-1-0115

SENIOR RESEARCH PERSONNEL: none, other than P.I.

JUNIOR RESEARCH PERSONNEL: D. W. Arnold, C. C. Arnold, S. E. Bradforth, E. de Beer, E. H. Kim, R. B. Metz, G. Reiser, T. Taylor, I. Yourshaw, A. Weaver, C. Xu, Y. Zhao

PUBLICATIONS ACKNOWLEDGING THIS GRANT: See attached

Abstract:

The research supported by this grant centers on the spectroscopy and dynamics of a variety of transient species including transition states, clusters, and free radicals. These species lie at the heart of many chemical processes, and our experiments have provided unprecedented insight into their nature. The novel feature of this program is that negative ion spectroscopy is used as the basic experimental tool in all of these experiments, because in many cases negative ions provide the only way to generate the transient species of interest in a reasonably well-defined manner. The projects described below fall into three categories: (a) spectroscopy of the transition state and reactive intermediates for neutral, bimolecular reactions, (b) the spectroscopy and electron detachment dynamics of carbon cluster anions, and (c) studies of size-selected, weakly bound anion and neutral clusters.

Technical Summary:

(A) Spectroscopy of the Transition State and of Reactive Intermediates

In these experiments, negative ion photoelectron spectroscopy is used to study the short-lived transition states characteristic of direct reactions or the longer lived reactive

intermediates that occur when the reaction coordinate involves one or more local minima. The idea is to access the neutral transition state or reactive intermediate by photodetachment of a suitable negative ion precursor, and the resulting photoelectron spectrum yields information on the vibrational structure and dissociation dynamics of the neutral complex.

The transition state regions of the $OH + OH \rightarrow O\,(^3P) + H_2O$ and the $OH + H_2O \rightarrow H_2O + OH$ reactions were studied by photoelectron spectroscopy of the $O^-(H_2O)$ and $H_3O_2^-$ anions and their deuterated analogs. The spectra show resolved vibrational progressions attributed to H-atom vibrational motion in the unstable neutral complexes formed by photodetachment. The positions and intensities of the peaks change markedly upon isotopic substitution. One dimensional Franck-Condon calculations using *ab initio* potentials for the anion and neutral are used to interpret the peak spacings and intensities, as well as the strong isotopic effects. The results can be understood in the context of previously obtained transition state spectra for heavy + light-heavy reactions.

The transition state region of the reaction $OH + H_2 \rightarrow H_2O + H$ was investigated by photoelectron spectroscopy of the H_3O^- and D_3O^- anions. The peaks observed in the spectra are from a combination of vibrational progressions and overlapping anion $\rightarrow$ neutral electronic transitions. The photoelectron angular distributions indicate that two processes contribute the spectra; these are assigned to photodetachment from the $H^-(H_2O)$ and $OH^-(H_2)$ forms of the anion. A comparison of experiments performed in two different laboratories shows that the two forms of the ion readily interconvert, and that the relative populations are determined solely by the temperature of the ions. In order to interpret the spectra, a two-dimensional *ab initio* potential energy surface for the anion was constructed, wavefunctions for the first few vibrational levels were determined, and the photoelectron spectra were simulated using the Walch-Dunning-Schatz-Elgersma surface for the $OH + H_2$ reaction. A comparison of the experimental and simulated spectra showed that photodetachment from the v=0 level of the anion, which is localized in the $H^-(H_2O)$ well, primarily probes the $H + H_2O$ exit valley of the neutral surface. The v=2

level of the anion is the first with significant amplitude in the $OH^-(H_2)$ well, and photodetachment from this level probes the $OH + H_2$ transition state region. The simulated spectra are in qualitative agreement with the experimental spectra, but do indicate that the neutral reactive surface needs to be modified.

In order to characterize the N_2O_2 reactive intermediate, photoelectron spectra of the $N_2O_2^-$ anion were obtained. The spectra originate from the C_{2v} isomer of the anion. Vibrationally resolved progressions corresponding to transitions to several electronic states of the previously unobserved N_2O_2 molecule are observed. All of the observed transitions lie above the dissociation asymptotes for $N_2 + O_2$, NO + NO, and $O + N_2O$, and several lie above the $N + NO_2$ and $N_2 + O + O$ asymptotes. *Ab initio* calculations have been carried out for the anion ground state and several singlet and triplet states of neutral N_2O_2. By comparing the observed spectra with Franck-Condon simulations based on these calculations, the lowest bands observed in our spectra were assigned to transitions to the $^3A_2$ and $^3A_1$ states (C_{2v} symmetry) of N_2O_2. These spectra thus represent the first experimental characterization of metastable, high energy forms of N_2O_2. Both the $N_2O_2^-$ and the N_2O_2 species are of interest due to their roles as reactive intermediates in the $O^- + N_2O$ and $N + NO_2$ chemical reactions.

Finally, the formyloxyl radical, HCO_2, was experimentally identified for the first time by photoelectron spectroscopy of HCO_2^- and DCO_2^-. Photodetachment accesses the $^2A_1$, $^2B_2$, and $^2A_2$ states of the formyloxyl radical, HCO_2. The $^2A_1$ state is assigned as the HCO_2 ground state, although it is nearly degenerate with the $^2B_2$ state (T_0=0.027 eV), and the $^2A_2$ state lies at T_0=0.536 eV. The electron affinity of HCO_2 is 3.498 ± 0.015 eV. The spectra show partially resolved vibrational features, primarily involving progressions in the CO_2 bending mode. The irregular appearance of the spectra in some regions suggests vibronic coupling between the $^2A_1$ and $^2B_2$ states. The possible role of the HCO_2 radical as an intermediate in the $OH + CO \rightarrow H + CO_2$ reaction and in $H + CO_2$ inelastic scattering is discussed.

B) Spectroscopy and Electron Detachment Dynamics of Carbon Cluster Anions.

We demonstrated for the first time that stimulated Raman pumping (SRP) can be used to vibrationally excite gas-phase negative ions. In SRP, a molecule or ion is excited by its interaction with two laser pulses whose frequencies differ by a vibrational quantum. This was achieved for C_2^-, in which stimulated Raman pumping excites a rotationally-resolved transition between the v=0 and v=1 levels of the ground $^2\Sigma_g^+$ state. The resulting vibrational excitation is monitored by resonant two-photon detachment through the excited B $^2\Sigma_u^+$ state. At least 35% conversion to the v=1 level was achieved in this study. It is expected that this method is quite generally applicable and will provide an excellent tool for the study of the vibrational spectroscopy of negative ions.

We have also studied the electronic spectroscopy of mass-selected carbon cluster anions using resonant multiphoton detachment spectroscopy. The C $^2\Pi_u \leftarrow$ X $^2\Pi_g$ electronic transition of C_4^- was studied by both one-color and two-color resonant two-photon detachment (R2PD) spectroscopy. The one-color spectrum reveals vibrational structure in the excited anion state. Transitions due to excitations in one of the symmetric stretching modes as well as the bending modes are observed. Spectral resolution in the one-color experiment is limited by power broadening; using two-color R2PD, rotationally resolved spectra of the origin and 2_0^1 bands of the C $^2\Pi_u \leftarrow$ X $^2\Pi_g$ transition are obtained. Molecular constants determined by fitting the rotationally-resolved spectra are generally in good agreement with a recent *ab initio* calculation by Schmatz and Botschwina. Perturbations in the 2_0^1 band are attributed to Fermi resonance interactions in the C $^2\Pi_u$ state.

Resonant multiphoton detachment spectroscopy was also used to obtain vibrationally resolved spectra of the C $^2\Pi_u \leftarrow$ X $^2\Pi_g$ electronic transitions in C_6^- and C_8^-. Transitions due to vibrational excitations in the totally symmetric stretching modes as well as the bending modes are observed. The electron detachment dynamics subsequent to multiphoton absorption were studied by measuring the electron emission time profiles and electron kinetic energy distributions. The observation of delayed electron emission combined with the form of the electron kinetic energy

distributions indicates that these species undergo the cluster equivalent of thermionic emission. This interpretation is supported by comparing the experimental results to a microcanonical model for cluster thermionic emission.

C) Studies of Size-selected Weakly-Bound Anion and Neutral Clusters.

These experiments are aimed at understanding how the properties of anions and neutrals are affected by solvation with relatively weakly interacting atoms and molecules. By starting with negative ions, size-selection of the species of interest is straightforward, and photodetachment spectroscopy reveals how binding energies, geometries, and electronic state splittings vary with the number and composition of solvating species.

Photoelectron spectra were measured for the anions $X^-(CO_2)$, with X = I, Br, Cl and F. The vibrationally resolved spectra show that $I^-(CO_2)$, $Br^-(CO_2)$, and $Cl^-(CO_2)$ are primarily electrostatically bound clusters, although the charge-quadrupole interaction is strong enough to distort the CO_2 molecule by as much as 10° (in $Cl^-(CO_2)$. *Ab initio* calculations and electrostatic models are used to describe the geometry and bonding of these clusters. The photoelectron spectrum of is qualitatively different and shows transitions to both the $\tilde{X}\ ^2B_2$ ground and the $\tilde{A}\ ^2A_2$ first excited electronic states of the covalently bound FCO_2 radical. The previously unobserved $\tilde{A}\ ^2A_2$ state is measured to lie 0.579 eV above the ground state. Vibrational frequencies are assigned with the assistance of *ab initio* calculations. The FCO_2 heat of formation is determined to be $\Delta_f H°_{298}(FCO_2)$= -85.2 ± 2.8 kcal/mole. While both FCO_2^- and FCO_2 are more strongly bound than the other halide-CO_2 clusters, the C-F bonds are very weak relative to C-F bonds found in other halocarbon compounds.

These studies of binary clusters were followed by investigations of clusters in which a halide ion is complexed to multiple solvent molecules. Specifically, photoelectron spectra of the $I^-(CO_2)_{n=1-13}$, $I^-(N_2O)_{n=1=12}$, and $Br^-(CO_2)_{n=1-11}$ clusters were obtained. The spectra provide information about the stepwise solvation of the bromide and iodide anions and about the size of the first solvation shells in these clusters. The data suggest that significantly different solute-solvent

interactions exist in the three sets of clusters studied here. The $X^-(CO_2)_n$ spectra exhibit resolved progressions which are assigned to in-phase CO_2 solvent bending vibrations in the neutral clusters. These vibrations are excited by photodetachment of anion clusters in which the CO_2 molecules are distorted from linearity by a charge-quadrupole interaction. The $I^-(N_2O)_n$ spectra do not show any vibrational structure, presumable because the weaker ion-solvent interactions are insufficient to distort the N_2O molecules.

Finally, the anion zero electron kinetic energy (ZEKE) spectra of the van der Waals clusters $Ar_{2-3}Br^-$ and $Ar_{2-7}I^-$ were measured, and partially discriminated threshold photodetachment (PDTP) experiments were been performed on $Ar_{4-9}Br^-$ and $Ar_{8-19}I^-$. The experiments yield size-dependent adiabatic electron affinities (EAs) and electronic state splittings of the halogen atom in the neutral clusters formed by photodetachment. These results are compared with simulated annealing calculations using model potentials for the anion and neutral clusters, making use of the neutral and anion pair potentials determined from previous work on the diatomic rare gas-halide atom complexes. A simple first-order degenerate perturbation theory model of the neutral cluster potentials was found to agree well with the size-dependent splitting of the halogen $^2P_{3/2}$ state observed in the ZEKE spectra. However, the binding energies calculated from the pair potentials alone were found to be inconsistent with the experimental electron affinities, and it was necessary to include various non-additive terms in the simulated annealing calculations to obtain reasonable agreement with experiment. Many-body induction in the anion clusters was found to be the dominant non-additive effect. The exchange quadrupole effect — i.e., the interaction of the exchange induced electron charge distribution distortion among argon atoms with the halide charge — was also found to be important. This comparison between experiment and theory provides a sensitive probe of the importance of non-additive effects in weakly bound clusters.

PUBLICATIONS:

1. C. C. Arnold D. M. Neumark, D. M. Cyr and M. A. Johnson, "Negative Ion Zero Electron Kinetic Energy Spectroscopy of $I^-{\bullet}CH_3I$," J. Phys. Chem. 99, 1633 (1995).

2. D. W. Arnold, S. E. Bradforth, E. H. Kim and D. M. Neumark, "Study of $I^-(CO_2)_n$, $Br^-(CO_2)_n$ and $I^-(N_2O)_n$ Clusters by Anion Photoelectron Spectroscopy," J. Chem. Phys. 102, 3510 (1995).

3. D. W. Arnold, S. E. Bradforth, E. H. Kim and D. M. Neumark, "Study of Halogen-Carbon Dioxide Clusters and the Fluoroformyloxyl Radical by Photodetachment of $X^-(CO_2)$[X = I, Cl, Br] and FCO_2^-," J. Chem. Phys. 102, 3493 (1995).

4. D. M. Neumark, "Studies of Transient Species Using Negative Ion Photodetachment," in Proceedings of The Robert A. Welch Foundation, 38th Conference on Chemical Research, Chemical Dynamics of Transient Species, (Robert A. Welch Foundation, Houston, TX, 1995).

5. D. W. Arnold, C. Xu and D. M. Neumark, "Spectroscopy of the Transition State: Elementary Reactions of the Hydroxyl Radical Studied by Photoelectron Spectroscopy of $O^-(H_2O)$ and $H_3O_2^-$," J. Chem. Phys. 102, 6088 (1995).

6. D. W. Arnold and D. M. Neumark, "Study of N_2O_2 by Photoelectron Spectroscopy of $N_2O_2^-$," J. Chem. Phys. 102, 7035 (1995).

7. E. de Beer, E. H. Kim, D. M. Neumark, R. F. Gunion and W. C. Lineberger, "Transition State Spectroscopy of the $OH + H_2 \rightarrow H_2O + H$ Reaction *via* Photodetachment of H_3O^- and D_3O^-," J. Phys. Chem. 99, 13627 (1995).

8. E. de Beer, Y. Zhao, I. Yourshaw, and D. M. Neumark, "Stimulated Raman Pumping of C_2^- Probed *via* Resonant Two-Photon Detachment," Chem. Phys. Lett. 244, 400 (1995).

9. E. H. Kim, S. E. Bradforth, D. W. Arnold, R. B. Metz, and D. M. Neumark, "Study of HCO_2 and DCO_2 by Negative Ion Photoelectron Spectroscopy," J. Chem. Phys. 103, 7801 (1995).

10. D. M. Neumark, "Probing the Transition State," in Physics News in 1995, ed. P. F. Schewe and B. P. Stein, (AIP, 1996) pp. 23-25.

11. D. M. Neumark, "Transition State Spectroscopy," Science 272, 1446 (1996).

12. I. Yourshaw, Y. Zhao, and D. M. Neumark, "Many-Body Effects in Weakly Bound Anion and Neutral Clusters: Zero Electron Kinetic Energy Spectroscopy and Threshold Photodetachment Spectroscopy of Ar_nBr^- (n=2-9) and Ar_nI^- (n=2-19)," J. Chem. Phys. 105, 351 (1996).

13. Y. Zhao, E. de Beer, and D. M. Neumark, "Rotationally Resolved Spectrum of the $C^2\Pi_u \leftarrow X^2\Pi_g$ Electronic Transition of C_4^- via Resonant 2-Photon Detachment Spectroscopy," J. Chem. Phys. 105, 2575 (1996).

14. Y. Zhao, E. de Beer, C. Xu, T. Taylor, and D. M. Neumark, "Spectroscopy and Electronic Detachment Dynamics of C_4^-, C_6^-, and C_8^-," J. Chem. Phys. 105, 4905 (1996).